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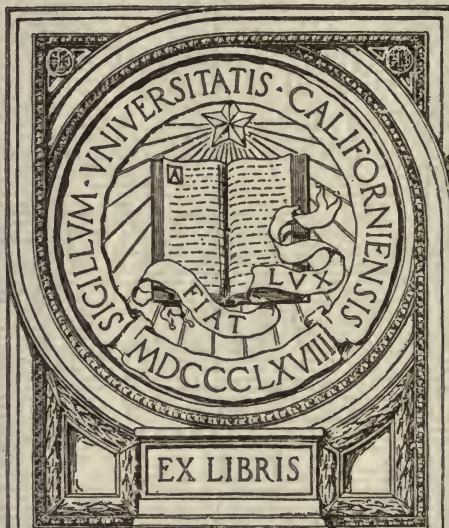
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I. The Three Nitro-Triphenylamines
II. The Oxidation of Diaminophenols

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

LOUIS MELVIN LARSEN

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CHICAGO, ILLINOIS
1921

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THE THREE NITRO-TRIPHENYLAMINES.*

(I) Theoretical Part.

Hitherto, only one mono-nitro derivative of triphenylamine has been known; it was prepared by Herz¹ in the year 1890 by the treatment of triphenylamine with nitric acid. Although this method of preparation contains no proof as to whether it is an ortho, a meta, or a para derivative it was, nevertheless, listed in the literature as the para. For a purpose,² which will be discussed later, Piccard and Kharasch needed the *p*-nitro-triphenylamine. Since we could not find in the literature any proof for the constitution of the compound prepared by Herz,³ nor a general method for the preparation of the nitro-triphenylamines, we tried to prepare *p*-nitro-triphenylamine by the introduction of phenyl groups into *p*-nitraniline. The substance thus produced was indeed identical with the product prepared by Herz. Against our proof, however, the objection could be raised, that a rearrangement might have taken place in the course of the reaction (heating for 30 hours at 200° in the presence of potassium carbonate). Were this last objection valid, then we could not obtain, when starting from the three mono-nitranilines, three different mono-nitro-triphenylamines. Hence we phenylated *o*- and *m*-nitraniline as well as *p*-nitraniline, and obtained three isomeric mono-nitro-triphenylamines. Absolute proof is thus given that our three derivatives are, respectively, the ortho, the meta, and the para compounds.

Irma Goldberg⁴ has introduced the use of phenyl iodide for the preparation of triphenylamine and some of its substitution derivatives. She heated diphenylamine with phenyl iodide and potassium carbonate in nitrobenzene solution in the presence of some copper powder. The latter had already been used for similar condensations as a catalytic reagent. Since Kahlbaum had introduced under the name "Kupferbronze" or "Naturkupfer C," a very good preparation made by powdering metallic copper in a special manner, no one in the past, it seems, prepared the cop-

* This work was published by Jean F. Piccard and Louis M. Larsen in the *Journal of the American Chemical Society*, **39**, 2006-2009 (1917).

¹ *Ber.*, **23**, 2537 (1890).

² For the identification of nitroso-triphenylamine.

³ When this article was ready for publication, we happened to find that Gamborian (*Ber.*, **41**, 3510 (1908)) had already prepared the *p*-nitro-triphenylamine by heating together diphenylamine and *p*-iodo-nitrobenzene from which it follows that its structure is the para. This reference is not given in Richter's "Lexikon" of 1911.

⁴ Irma Goldberg, when making *o*-nitro-diphenylamine by heating in this manner *o*-nitraniline with phenyl iodide, obtained, in addition to tarry by-products, a mixture consisting of unchanged *o*-nitraniline, *o*-nitro-diphenylamine, and *o*-nitro-triphenylamine. She did not, however, isolate the last substance. *Ber.*, **40**, 4542 (1907).

per powder for himself. Being unable to secure at this time the German product, we tried a new chemical method for making it, and we are glad to say that it is possible to make in this country a copper powder, which is equal, if not superior, to the German standard.

(2) Experimental Part.

A. The Preparation of Catalytic Copper.—A solution of chromous chloride was prepared by the reduction of 190 g. of commercial sodium dichromate by means of an excess of pure zinc (600 g.) in the presence of 1250 cc. of concentrated hydrochloric acid. The acid was added in three portions. The reaction was vigorous, generating much heat with the evolution of much steam, acid and hydrogen. The color changed first to a green and finally to a light blue. When the reaction had subsided and the reduction was complete, the mixture was freed from zinc by filtration through glass wool. The chromous chloride was protected from oxidation by a rapid current of carbon dioxide. The solution was now rapidly cooled.

A solution of 120 g. of crystallized copper sulfate in 700 cc. of water was prepared and, shaken well, cooled in a freezing bath until it had become filled with a mass of ice crystals. The mixture was now poured into the chromous chloride with proper stirring. The reduction is quantitative and instantaneous. The precipitated copper was washed by decantation with much water, then with absolute alcohol, then transferred to a suction filter and washed with benzene and finally with a solution of vaseline in benzene. The vaseline prevents oxidation by the air and makes the preparation quite stable. The yield is theoretical.

The copper thus prepared forms a light red powder, which is exceedingly finely divided, without any metallic luster. Rubbed between the fingers, it remains on the skin like flour.

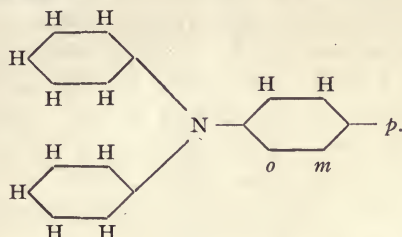
For catalytic purposes in the phenylation of aromatic amines the copper may be used alone or it may be mixed with a small amount of potassium iodide as recommended by Irma Goldberg.¹

B. The Preparation of the Three Nitro-triphenylamines.—For the preparation of a nitro-triphenylamine by phenylation, we can start directly from the respective nitraniline. First one phenyl group is introduced and the nitro-diphenylamine formed reacts then with a second molecule of phenyl iodide. In this manner we get in addition to unchanged nitraniline and nitro-diphenylamine, the nitro-triphenylamine together with a quantity of tarry by-products. As the nitro-triphenylamine has no basic properties, its isolation and purification is a disagreeable piece of work. We find that the tarry products are only formed during the first step of the reaction, they are derivatives of the nitraniline and not of the nitro-di- or the nitro-triphenylamines. For this reason it is better to make first in one way or

¹ *Ber.*, 40, 4542 (1907).

another a pure nitro-diphenylamine and then phenylate this. We have then but to isolate the nitro-triphenylamine from a nitrobenzene solution which contains only a very small amount of unchanged nitro-diphenylamine, if any, no nitraniline and no tar.

Nitro-triphenylamines.—



Two grams of pure *p*-nitro-diphenylamine, 5 cc. of phenyl iodide, 0.7 g. of potassium carbonate, about 0.1–0.2 g. of copper powder mixed with a little potassium iodide, were boiled together with 10 cc. of nitrobenzene under a reflux condenser for 30 hours on a sand bath. The excess of phenyl iodide and of nitrobenzene was removed by steam distillation. The mixture remaining was extracted with ether and the extract filtered. After due removal of the ether and after cooling, the residue crystallized. Any unchanged *p*-nitro-diphenylamine was completely removed by treatment with warm concentrated hydrochloric acid. The *p*-nitro-triphenylamine was recrystallized from 50% alcohol. The pure substance melted at 140° and when mixed with the product of direct nitration of triphenylamine,¹ no depression was observed. Thus, the direct nitration gives the para product. The statement that decomposition occurs at the melting point is incorrect. The crude yield (m. p. 133°) was 94% of the theoretical.

Pure *m*-nitro-diphenylamine (2 g.) was heated at boiling for 30 hours, together with 5 cc. of phenyl iodide, 0.7 g. of potassium carbonate, about 0.2 g. of copper mixed with a little potassium iodide, and 10 cc. of nitrobenzene. The mixture acquired a lighter color as the reaction went on. The excess of phenyl iodide and nitrobenzene was removed by a steam distillation. After treatment with concentrated hydrochloric acid, the crude light yellow residue was recrystallized from dilute alcohol and also from methyl alcohol. The crude product melted at 75–76° and the pure product at 78°. Recrystallization from acetic acid did not change the melting point. The crude yield was about 95% and only a few per cent. were lost during further purification.

Subst. 0.1120; CO₂, 0.3044; H₂O, 0.0500.

0.0674; CO₂, 0.1837; H₂O, 0.0307.

0.2833; 24.9 cc. dry N₂ at 22° and 726 mm.

Calc. for C₁₈H₁₄O₂N₂: C, 74.46; H, 4.86; N, 9.66. Found: C, 74.14, 74.36; H, 4.99, 5.10; N, 9.72.

¹ M. p. 139–140° according to Herz.

The *m*-nitro-triphenylamine is lemon-yellow similar to *m*-nitraniline; both differ from the *m*-nitro-diphenylamine, which is brick-red. It is very soluble in nitrobenzene, benzene, ether, and ethyl acetate; moderately soluble in alcohol, insoluble in water and acids. However, it is quite soluble in glacial acetic acid and in concentrated sulfuric acid. The latter solution at first is colorless, but acquires a blue coloration in a few seconds.

Pure *o*-nitro-diphenylamine (2 g.) was phenylated in the same manner as the corresponding *m*-derivative. Here also the reaction is quantitative. The crude product, 2.6 g., melted at 96°. After several recrystallizations from alcohol, the melting point rose to 98° and there remained constant. Recrystallizations from ethyl alcohol did not change the melting point. The crude yield was 95% of the theoretical.

Subst. 0.1343; CO₂, 0.3656; H₂O, 0.0609.

0.2180; 18.5 cc. dry N₂ at 21° and 734 mm. (CuO).

0.1051; 9.35 cc. dry N at 21° and 725.5 mm. (PbCrO₄).

Calc. for C₁₈H₁₄O₂N₂: C, 74.46; H, 4.86; N, 9.66. Found: C, 74.27; H, 5.07; N, 9.52, 9.87.

The *o*-nitro-triphenylamine is yellow-orange in color. In large crystals it is orange-brown. Its properties are very similar to those of the already described para and meta derivatives.

II.

THE OXIDATION OF DIAMINOPHENOLS.*

Theoretical Part.

That diaminophenols on oxidation give red solutions is known to all who have worked with these substances. F. Kehrmann and H. Prager¹ succeeded in isolating some of these oxidation products and recognized them as salts of holoquinoid² aminoquinonimines. Some years later, Jean Piccard³ re-investigated these compounds; by titration and by reduction to the original leucobase he confirmed the formulas given by Kehrmann and Prager. On the other hand, he compared the absorption spectra with those of the meriquinoid salts,⁴ selecting such representatives as the

* Published by Jean F. Piccard and Louis M. Larsen in the *Journal of the American Chemical Society*, **40**, 1079-1092 (1918).

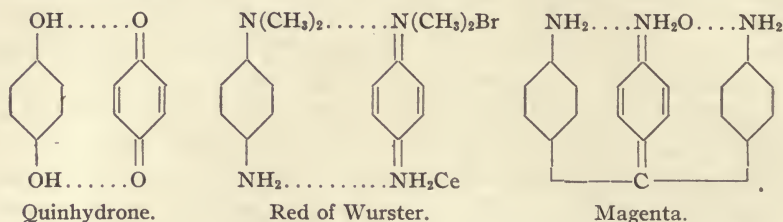
¹ *Ber.*, **39**, 3438 (1906).

² Holoquinoid is applied to those aromatic compounds which possess the quinoid structure. Quinone, $O = C_6H_4 = O$, is a common example. Meriquinoid is applied to those quinonimine salts, whose C_6 rings are (as in quinhydrone) partly quinoid and partly hydroquinoid. Red of Wurster and magenta, shown above, are examples of this class. They have always a very pronounced color and are considered as the mother substances of most of the dyes. (Willstätter and Piccard, *Ber.* **41**, 1465 (1908)).

³ *Ber.*, **42**, 4339 (1909).

⁴ A part of this work was done by Dr. Piccard in the Chemical Laboratory of the Royal Academy of Sciences in Munich in 1912 but has not previously been published.

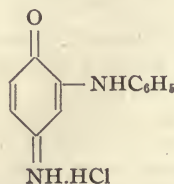
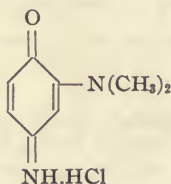
Red of Wurster (intermolecular meriquinoid) and magenta (intramolecular meriquinoid).



He found that the new class of substances, although highly colored when compared with the colorless quinonimine salts, are, however, far from attaining the color brilliancy and intensity of the true meriquinoid salts. The latter possess characteristic absorption bands, while the former show only a general absorption in the violet region of the spectrum.

Later, from the work of F. Kehrman and St. Micewicz¹ and of Piccard² it became known that the substitution of a phenyl-immonium group for the dimethyl-immonium group produces in the case of the simple holoquinoid salts a great lowering³ of color, while in the meriquinoid salts only a very slight change is produced. Thus tetramethylphenyldiamine (CH₃)₂-N-C₆H₄-N(CH₃)₂ gives blue meriquinoid and *colorless* holoquinoid salts, while phenyldimethylphenyldiamine (CH₃)₂-N-C₆H₄-NHC₆H₅ and diphenylphenyldiamine C₆H₅NH-C₆H₄-NHC₆H₅ whose meriquinoid salts are also blue, gives *red* holoquinoid salts.

These interesting relations were not at all expected. We decided to investigate the aminoquinonimine salts similarly and their preparation is the object of our present work. New quinoid salts were prepared from 2,4-diaminophenol (I), 2-dimethylamino-4-aminophenol (II), and 2-phenylamino-4-aminophenol (III). *We find that in this class of substances the usual rule holds, e. g., a phenylamine group has approximately the same effect as the dimethylamine group.*



Dimethylaminoquinonimine salts give violet-red solutions and phenylaminoquinonimine salts have the same color.

¹ *Ber.*, **45**, 2651 (1912).

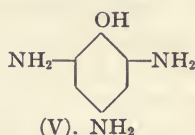
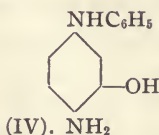
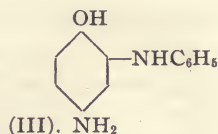
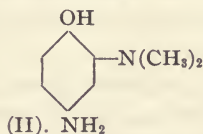
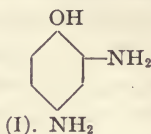
² *Ibid.*, **46**, 1850 (1913).

³ We call yellow the highest color, from which we go through orange, red, violet and blue to green, which is then the lowest color.

Kehrmann and Prager¹ oxidized the 2,4-diaminophenol (I) as well as a number of its homologs, (diamino-*o*-cresol, diamino-*m*-cresol, diamino-thymol) and isolated holoquinoid salts either as nitrates or picrates, or as bichromates. From the last base they prepared a chloride, a double salt with mercury chloride, and an oxalate; but these were neither analyzed nor studied further. Since the analyzed salts prepared by Kehrmann and Prager are unsuitable for titration, Piccard² isolated and titrated the quinoid hydrochloride of diamino-*o*-cresol. Its constitution was definitely shown to be holoquinoid.

Since the simplest of the substances under investigation, *e. g.*, the amino-quinonimine has been known only as the picrate and the bichromate, both unsuitable for titration, we sought the salt of a colorless monobasic acid³ which can be easily titrated. After several attempts we succeeded in isolating and studying the properties of the rather unstable and easily soluble hydrochloride.

We then turned our attention to the oxidation of the corresponding dimethyldiamino—(II) and the phenyldiamino—(III) phenols, so that a comparison of the colors of the oxidation products could be made, this being the primary object of this paper.



The desired dimethyldiaminophenol (II) was already known.⁴ The known phenyldiaminophenol⁵ (IV) does not possess the desired constitution. Therefore we tried the preparation of the 2-phenylamino-4-aminophenol (III).

Gattermann⁶ has shown that when an aromatic nitro-compound is reduced electrolytically in strong sulfuric acid, a *p*-aminophenol is produced. Thus from nitrobenzene he prepared the *p*-aminophenol, from *m*-nitraniline

¹ *Ber.*, 39, 3438 (1906).

² *Ibid.*, 42, 4339 (1909).

³ The salts of hydrochloric and perchloric acids are desirable because these acids are themselves colorless and do not, as do nitric, chromic, sulfuric, and picric acids, interfere with the titration.

⁴ L. Gattermann, *Ber.*, 27, 1932 (1894).

⁵ L. Kohler, *Ibid.*, 21, 910 (1888).


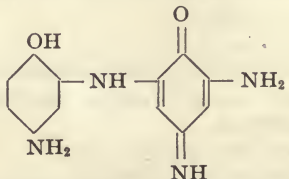
⁶ *Ber.*, 26, 1847 (1893).

the 2,4-diaminophenol (I), and from *m*-nitrodimethylaniline the 2-dimethylamino-4-aminophenol (II).

We now applied the reduction, introduced by Gattermann, to the *m*-nitrodiphenylamine, (*m*-nitrophenylaniline). For determining whether or not the phenyldiaminophenol was formed and for following the course of the reaction the same test was here used which was employed in detecting the presence of the diaminophenol and the dimethyldiaminophenol during their preparation. A test portion (0.1 cc.) of the reaction mixture was removed, diluted with 5 cc. water, filtered from any unchanged nitro-compound and sulfur (formed from the reduction of some of the acid), and then oxidized with a dilute solution of ferric chloride. The formation of a red solution in the case of the reduction of the *m*-nitraniline showed that the 2,4-diaminophenol was formed; similarly in the case of the *m*-nitrodimethylaniline a violet-red solution was formed. In the case of the reduction of the *m*-nitrodiphenylamine, a violet-red coloration was produced. The isolation of the reduction product is described later. Its properties and analysis together with the manner of preparation show that it is indeed the desired 2-phenylamino-4-aminophenol (III).

On oxidation the two phenyl-diaminophenols gave similar violet-red solutions. The isolation of the oxidation product of the phenyldiaminophenol (III) as the hydrochloride, the nitrate, and the perchlorate was unsuccessfully attempted. These salts were found to be too soluble and also unstable in the concentrated solutions, rapidly forming condensation products. We prepared the picrate for analysis. For observations on the color of the oxidation product freshly prepared dilute solutions of the hydrochloride, which need not be isolated in the solid condition, were employed.

The oxidation of leucobase may give rise to holoquinoid, meriquinoid, or to condensation products. Usually, it is not necessary to isolate the product in order to determine whether or not condensation has taken place. A suitable amount of the substance in excess is oxidized by a standard solution of an oxidizing agent, and the resulting colored solution is titrated to the disappearance of color by a standard solution of a reducing agent. If equivalent amounts of the reagents are required, no condensation has taken place; but if less than an equivalent amount of the reducing reagent is needed, a condensation or a substitution¹ has taken place. On oxidation of

of  2 molecules of the leucobase require 2 atoms of oxygen. After condensation to , for instance,

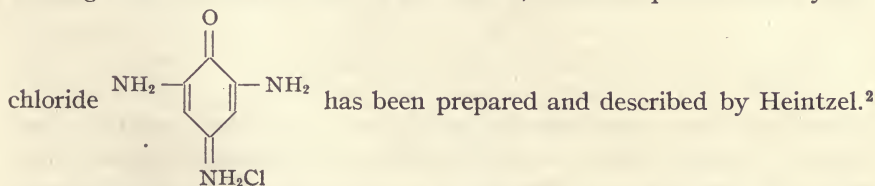
¹ If a halogen is used as the oxidizing agent, substitution may readily take place.

only 2 atoms of hydrogen would be required for reduction. But when the right conditions (temperature, concentration, oxidizing agent, etc.) were chosen, experiment showed that 4 atoms of hydrogen were required for decolorization, showing that no appreciable condensation has taken place.¹ This method was applied to each of the diaminophenols to ascertain whether or not a condensation takes place during the oxidation. In each case it was found that the first product of oxidation is not one of condensation, but that condensation may take place afterwards, less readily when the solution is made more dilute and when it is cooled.

Two methods are used to determine whether the product of oxidation is holoquinoid or meriquinoid. One method consists in oxidizing equal amounts of the leucobase, whose molecular weight and number of hydroquinoid nuclei are known, with different amounts of a standard solution of an oxidizing agent until the maximum intensity of the color is reached. If *one* atom of oxygen for every hydroquinoid nucleus is needed for this oxidation, the product is *holoquinoid*, but if *less* than this amount is needed (usually $\frac{1}{2}$ or $\frac{1}{3}$), the product is *meriquinoid*. The other method, applicable only when the oxidation product has been isolated, consists in the titration of a known amount of the latter, whole molecular weight must be known, to the disappearance of color with a standard solution of a reducing agent. From these data the constitution of the substance is readily determined.

Both methods, applied to the aminophenols (I to V inclusive), showed that these substances form holoquinoid, not meriquinoid, salts on oxidation.

The introduction of one auxochromic amino group into quinonimine is accompanied by a change of the color of the solution from almost colorless to red. The addition of strong acid to this red solution changes it to a pale yellow, due to salt formation with the auxochrome group. The introduction of one more amino group into the quinonimine is accompanied by a change of the color from red to blue: the 2,6-diaminoquinonimine hydro-



The addition of strong acid changes the blue solution to a red, one of the two auxochrome groups being neutralized and the effect produced is the same as if that group were entirely eliminated.

The aminoquinonimine salts, as a class, differ considerably from the tri-

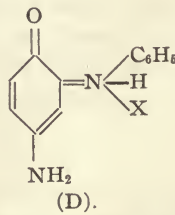
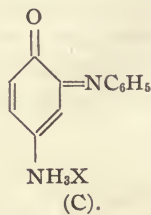
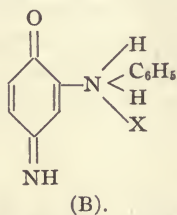
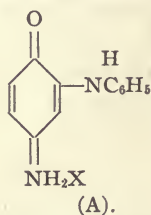
¹ Not too concentrated solutions were employed here, for the oxidation is followed by condensation reactions, which had to be avoided as much as possible.

² *Z. Chem.*, 1867, 342.

phenylmethane dyes in that they are much less brilliant than the latter, and also in that they lose the color intensity in decreasing thickness of layers, more rapidly than do the latter; a 0.004% solution of the dimethylaminoquinonimine perchlorate when viewed laterally through a tube, 1.5 cm. in diameter, was exactly matched by a 0.001% solution of triphenylmethane dyes (made by mixing 10 cc. of a 0.001% solution of crystal violet with 100 cc. of rosaniline acetate of the same strength), but when viewed through a layer of 20 cm. the quinonimine solution was much deeper in color. On the other hand through a layer of 0.25 cm. thickness it was lighter. Through the spectroscope the triphenylmethane dyes at the above concentration showed very pronounced absorption bands through a thickness of 1.5 cm., whereas the quinonimine, even when considerably more concentrated, showed no appreciable absorption bands whatever.

The absorption spectra of the dimethylamino- and the phenylaminoquinonimine salts show only general absorption in the green and the green-blue regions of the spectrum. The former are characterized by a slightly sharper absorption curve and are thus slightly more brilliant than the latter. Also, their color, with decreasing thickness of layers, decreases a little more slowly than that of the latter salts. Even the 2,6-diaminoquinonimine salts have no sharp bands but possess general absorption with a wide maximum in the orange. These lose their intensity like the salts of the other quinonimines (holoquinoid).

Although we are unable to say with certainty whether the structure of these compounds is para- or orthoquinoid, still we are led to believe that the former (A) is correct. The following gives the possible formulas for the holoquinoid phenylamino derivative:



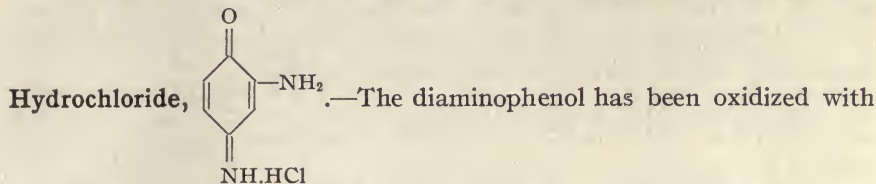
Formula C is impossible for the special case of the dimethylamino compound. Formulas B and C are both unlikely for all cases because no auxochrome group¹ is present. Formula A is preferable to D because the imino group (=NH) is more basic than the phenylimino group (=NC₆H₅). Formula A has also become accepted for the dimethylamino derivative, but for this substance no definite proof has yet been found against the constitution D.

The solutions of our compounds could also involve an equilibrium between different forms.

¹ The group (—NR₂X) is not an auxochrome group.

Experimental Part.

1. Oxidation of 2,4-Diaminophenol (I). A. Preparation of the Quinoid



ferric chloride by Kehrman and Prager.¹ They prepared the hydrochloride by shaking the reaction mixture with solid sodium chloride, but they were unable to separate the easily soluble hydrochloride from excess of sodium chloride. Since the salts prepared and analyzed by them are unsuitable for titration, we tried to prepare the pure hydrochloride.

We observed that the hydrochloride is quite unstable in concentrated solutions. A strong aqueous solution, even at 0° changes within a few seconds, forming brown condensation products. Thus it becomes absolutely necessary in its isolation to avoid washing the salt with pure water. For this reason, attempts were made to precipitate the salt with a concentrated solution of calcium chloride, the latter being washed out with absolute alcohol. In this manner we obtained an excellent yield, but on ignition some ash remained.

On the other hand, a slight excess of ferric chloride may be used to precipitate the salt in concentrated solutions. If too concentrated, the leucohydrochloride precipitates before its oxidation becomes complete. The method described below gave us a preparation whose ash was negligible. We sacrificed the yield in this and other preparations in order that the products might be obtained directly in pure condition.

Four g. of pure recrystallized 2,4-diaminophenoldihydrochloride² in 50 cc. water at 0° was oxidized by 20 cc. of a 4 N ferric chloride solution (650 g. sublimed ferric chloride per liter of solution) cooled to 0°. The deep red solution was further cooled and held at -15° for 15 minutes. The formation of red crystals was noted after a few moments of vigorous rubbing. The precipitate was collected on a suction filter, washed with cold absolute alcohol (-20°) and with absolute ether. By keeping the substance covered with absolute ether, care was taken to prevent air currents from depositing moisture upon the substance. The presence of even small amounts of water causes it to turn brown and finally black. The preparation was dried to constant weight within 4 days, over sulfuric acid and soda-lime *in vacuo*. The yield was 50% of the theoretical.

For titration, the salt was dried only 6 hours. A suitable portion was dissolved rapidly in 50 cc. of water, acidified with 10 cc. of oxygen-free

¹ Ber., 39, 3437 (1906).

² L. Gattermann, *Ibid.*, 26, 1849 (1893).

normal acid, a small quantity of sodium fluoride¹ added, and titrated immediately with 0.03 *N* titanium trichloride in an atmosphere of carbon dioxide. At the end, the reduction was hastened by warming the solution to 40°. The endpoint was partly masked by the presence of a light brown coloration. Fair results were, nevertheless, obtained.

Subst., 0.1484; CO₂, 0.2481; H₂O, 0.0622. Subst., 0.1504; 23.25 cc. dry N₂ at 18° and 733 mm. Subst., 0.1906; 0.1721 AgCl. Subst., 0.0607, 0.0614, 0.0454; 25.70, 25.35, 19.20 cc. 0.03 *N* TiCl₃.

Calc. for C₆H₇ON₂Cl: C, 45.42; H, 4.45; N, 17.67; Cl, 22.36; H equiv., 79.25.

Found: C, 45.61; H, 4.69; N, 17.50; Cl, 22.34; H equiv., 78.7, 80.7, 78.8.

This salt is shown by the titration to be holoquinoid. Condensation products and meriquinoid salts of the same composition would require less hydrogen for reduction.

In reflected light the preparation shows some green surface color and when rubbed to thin layers on a watch glass, the salt appears violet-red.

This salt crystallizes in 2 forms: a light one, consisting of light red needles, without any complementary surface color, and a dark one, consisting of plates, with a green surface color. The light form soon changes into the stable dark modification. This occurs rapidly when a portion of the mother liquor, in which the light red needles are suspended, is seeded with a little of the dark modification. The needles are observed, under the microscope, to go back into solution and the dark plates, being less soluble, precipitate out. We have not been able to isolate the light modification of the chloride. But in the case of the perchlorate and the nitrate, described below, the salts are light red without any complimentary surface color. These are then the light modifications. This curious phenomenon of 2 isomeric forms has been observed before in the preparation of other quinonimines.²

The earlier suggestion that the light and the dark forms possess the para and the ortho quinoid formulas has now been abandoned. They form identical solutions and are believed to be different states of aggregation.

When kept dry the salt is stable for a week or more. Acid solutions are far more stable than neutral ones. In dilute aqueous solution it is stable for several hours, but in concentrated solutions a rapid change occurs. This change is not due to hydrolysis but to a condensation reaction, for its velocity is markedly dependent upon concentration.³ If we place equal quantities (0.01 g.) of the salt in 2 dishes, rub one portion a few seconds with 0.5 cc. of water, and then throw both dishes, with stirring, into a

¹ J. Piccard, *Ber.*, **42**, 4343 (1909).

² *Ibid.*, **42**, 4338 (1909).

³ The velocity of multimolecular reactions is dependent upon the concentration, whereas the rate of hydrolysis is mono-molecular with respect to the substance and practically independent of concentration, if the latter is not too great.

liter of water each, the first forms a dark brown solution, while the second shows a brilliant wine-red coloration which only after several hours becomes brown.

The hydrochloride is readily soluble in water, soluble in alcohol but insoluble in acetone. Its solutions have a red color like that of ferric thiocyanate. On the addition of conc. sulfuric acid the red of the aminoquinonimine changes to a pale yellow, due to the absorption of a second acid equivalent by the auxochrome group. The solution on dilution becomes red again.

The spectrum shows general absorption in the violet region.

B. Preparation of the Quinoid Perchlorate and Nitrate.—Since the perchlorate of the dimethyl derivative, described below, was found by titration to be of high purity, we attempted the preparation of a perchlorate of aminoquinonimine in analogous manner. Beautiful, glistening light red needles were isolated, which when heated exploded violently, a common property of organic perchlorates. Analysis showed, however, that the preparation was not pure. Its ash was approximately 0.7% and chlorine determinations gave 16.65% and 16.60%, respectively. The value calculated in the pure perchlorate for chlorine is 15.93%.

As the solubility of the chloride is not much greater than that of the perchlorate, the preparation of the latter was attempted by using ferric nitrate, instead of ferric chloride. The salt obtained was, however, not a perchlorate but a nitrate. Further work on the perchlorate was dropped at this point, as this salt is not essential for our observations.

The yield of the nitrate was increased by the addition of a concentrated solution of sodium nitrate. The preparation obtained according to the following procedure, left no ash on ignition:

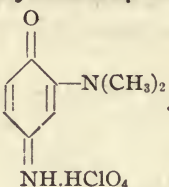
Two g. of pure recrystallized 2,4-diaminophenoldihydrochloride in 40 cc. water at 0° was oxidized by 20 cc. of 2 *N* ferric nitrate solution cooled to 0°. Crystallization of the nitrate began almost immediately. To the mixture, cooled to -15°, was added 20 cc. of a cold saturated solution of sodium nitrate. After 15 minutes, the precipitate was collected on a suction filter and rapidly washed with a little cold absolute alcohol (-20°), a little cold water (0°), considerable cold absolute alcohol and much dry ether. The preparation was dried *in vacuo*, requiring 4 days to attain constant weight. The yield was about 50% of the theoretical.

Subst., 0.1505; 2955 cc. dry N₂ at 15° and 735 mm.

Calc. for C₆H₇O₄N₃: N, 22.71. Found: 22.53.

The nitrate is easily soluble in water, somewhat soluble in alcohol and acetone, but insoluble in chloroform. It is not as readily blackened by moisture as is the chloride. Its properties are similar to those of the chloride. Only one modification was observed: long, bright red needles.

II. Oxidation of the 2-Dimethylamine-4-aminophenol. A. Preparation

of the Quinoid Perchlorate, .—A solution of 5 g. of pure

recrystallized 2-dimethylamino-4-aminophenol-di-hydrochloride¹ in 50 cc. water at 0° was oxidized by 25 cc. of a 4 *N* solution of ferric chloride at 0°. An intense violet-red coloration was produced. A solution of pure sodium perchlorate (30 cc.), saturated at 20°, was added to the reaction mixture. After a few moments, crystallization began. After being cooled at -20° for half an hour, the perchlorate was collected and washed successively with a saturated solution of sodium perchlorate at -20°, cold absolute alcohol, a few drops of ice-cold water, more cold absolute alcohol, and alcohol-ether mixture, and finally with much dry ether. The preparation was immediately placed in a desiccator and dried in the usual manner. Constant weight was obtained almost at once. The yield was 25-30% of the theoretical.

The chlorine determination was made by the following rapid and convenient method, introduced by K. Hofmann:² A suitable quantity of the material is intimately mixed in a platinum crucible with pure sodium carbonate (8 g.) and covered with more carbonate. To avoid loss of material resulting from too vigorous a reaction, we heated the top layers first. The organic matter is completely oxidized leaving an excess of sodium perchlorate, and the operation is complete only after this has been converted into the chloride. The cooled mass is dissolved in water, neutralized with dil. nitric acid, and the chlorine precipitated by silver nitrate.

For titration a suitable portion of the perchlorate was reduced with 0.03 *N* titanium trichloride, great care being taken not to overstep the end-point. The reduction was rather slow but complete. The solution showed no brown coloration whatever at the end-point. The values obtained show that this substance is holoquinoid, and also that it is very pure.

Subst., 0.1952, 0.2070; CO₂, 0.2742, 0.2891; H₂O, 0.0784, 0.0834. Subst., 0.2169, 0.3084; 21.15 cc. dry N₂ at 22° and 751 mm. 30.30 cc. dry N₂ at 24.5° and 748 mm. Subst., 0.2200, 0.2680; AgCl, 0.1273, 0.1528. Subst., 0.1107, 0.1122; 29.33, 29.75 cc. 0.03 *N* TiCl₃.

Calc. for C₈H₁₁O₃N₂Cl: C, 38.31; H, 4.42; N, 11.18; Cl, 14.15; H equiv., 125.3. Found: C, 38.32, 38.10; H, 4.49, 4.51; N, 11.16, 11.10; Cl, 14.31, 14.07; H equiv., 125.8, 125.7.

The perchlorate crystallizes in light red needles. Its solutions have a very beautiful violet-red color. Dilute solutions were found stable for

¹ L. Gattermann, *Ber.*, 27, 1932 (1894).

² K. Hofmann, A. Metzler and K. Hobold, *Ibid.*, 43, 1081 (1910).

several days. Condensation products are formed here too, but less readily than from the simple amino derivative (described above). The salt is readily soluble in water, quite soluble in alcohol, acetone, glacial acetic acid but insoluble in chloroform. Like the salts of the previous aminoquinonimine, its color is not changed by strong acids except concentrated sulfuric acid, in which it dissolves to a pale yellow solution. The latter solution on dilution again becomes violet-red.

The light red crystals were observed to change slowly on standing, becoming darker. Analysis showed that the chlorine content remained unchanged.

The absorption curve of the perchlorate is quite flat with a wide maximum in the green.

B. Preparation of the Picrate.—The picrates of the quinonimines are insoluble and can be prepared readily with a good yield. But due to hydrolysis and often to precipitation of picric acid in the acid solution, they are difficult to obtain in pure condition.

A solution of one g. of 2-dimethylamino-4-aminophenoldihydrochloride in 25 cc. water at 0° was oxidized by 5 cc. of a cold 4 *N* solution of ferric chloride. The resulting violet-red solution was added slowly to a cold solution of 2 g. picric acid in 350 cc. water. Crystallization took place immediately. The mixture was cooled, and the dark brown crystals were collected, washed with 25 cc. of cold dil. picric acid solution and about 20 cc. of ice cold water. The preparation was dried *in vacuo* to constant weight. The yield amounted to 90% of the theoretical.

Subst., 0.2256; CO₂, 0.3632; H₂O, 0.0718. Subst., 0.1619; 26.75 cc. dry N₂ at 21° and 736 mm.

Calc. for C₁₄H₁₃O₃N₃: C, 44.33; H, 3.45; N, 18.47. Found: C, 43.92; H, 3.56; N, 18.60.

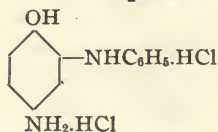
The picrate dissolves with a red color, readily in alcohol and acetone, sparingly in chloroform and water. When the salt is warmed with water, hydrolysis with subsequent decomposition occurs. It dissolves easily in acids giving violet-red solutions. It crystallizes in clusters of long needles.

III. Oxidation of 3-Phenylamino-6-aminophenol.—This phenol (IV) has been isolated and described by Kohler.¹ On oxidation with ferric chloride it gives solutions having the same violet-red color as those prepared from the preceding dimethyldiaminophenol. By oxidation and then by reduction we have been able to show that no appreciable condensation takes place, for equivalent amounts of standard solutions are used for both operations.

Salts of this quinonimine were not isolated, because we are now able to prepare the desired phenol (III) and from it the quinonimine picrate.

¹ *Ber.*, 21, 910 (1888).

IV. Preparation of 2-Phenylamino-4-aminophenol Dihydrochloride,



—Ten g. of *m*-nitrodiphenylamine¹ prepared by the

phenylation² of *m*-nitraniline were dissolved with gentle warming in 85 cc. of conc. sulfuric acid and reduced electrolytically.³ The average amperage and voltage for the 20-hour run were 1.5 and 6.5, respectively. Each electrode was of 15 sq. cm. surface. From time to time, test portions were removed, diluted, filtered from any unchanged nitro-compound, and oxidized by ferric chloride. During the reduction, the nitro-compound gradually disappeared and the violet-red coloration, formed in the test portion by oxidation with ferric chloride, became correspondingly more intense. After but little of the unchanged nitro-compound was left, the acid solution was filtered and then diluted with 500 g. of crushed ice. A red precipitate (2 g.) formed, from which a gram of unchanged *m*-nitrodiphenylamine was recovered. After filtration, the acid solution was neutralized by sodium carbonate and some sodium sulfite, the operation being completed with bicarbonate. The aminophenol was repeatedly extracted from the neutral solution with ether. The ether solution was clarified with anhydrous sodium sulfate, filtered and shaken well with an excess of dil. hydrochloric acid. The resulting acid solution was filtered and evaporated to dryness under reduced pressure in the absence of air. Crystals, slightly pink from oxidation, appeared toward the end. The product was powdered and dried *in vacuo*. The salt is very hygroscopic and when exposed to the air is rapidly oxidized, finally forming a dark brown product. The yield amounted to 7.8 g. Constant weight was not attained within 2 weeks due to a loss of hydrochloric acid and also to gradual oxidation. It then gave the following analysis:

Subst., 0.1600; CO₂, 0.3130; H₂O, 0.0776. Subst., 0.1626; 15.20 cc. dry N₂ at 20° and 724 mm. 0.1643; AgCl, 0.1605.

Calc. for C₁₂H₁₂ON₂·2HCl: C, 52.75; H, 5.16; N, 10.26; Cl, 25.97. Found: C, 53.24; H, 5.41; N, 10.57; Cl, 24.17.

The salt is very soluble in water, moderately soluble in alcohol and difficultly in glacial acetic acid. On being heated it turns brown. An aqueous solution forms on standing a dark amorphous precipitate, insoluble in dilute acids. Oxidized with a limited amount of bromine, phenylaminoquinonimine is produced; an excess of bromine precipitates a yellow sub-

¹ I. Goldberg, *Ber.*, 40, 4545 (1907).

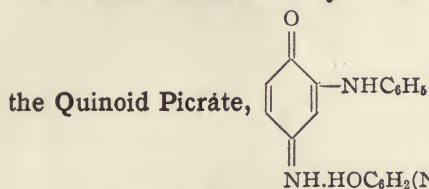
² In our first paper (*J. Am. Chem. Soc.*, 39, 2006 (1917)) we indicated in Footnote 3, page 2006 by mistake the name of Bamberger instead of Stefan Gambarian. The reference (*Ber.*, 41, 3510) was correct.

³ L. Gattermann, *Ber.*, 26, 1846 (1893).

stance. The coloration produced by ferric chloride is similar to that formed in the case of the dimethyl derivative and this solution is decolorized by conc. hydrochloric acid. This disappearance of color does not depend upon the formation of an acid salt but upon the fact that the ferrous salts present under these conditions reduce the quinonimine. This equilibrium is again shifted when water is added to the solution. Indeed the coloration produced by bromine is not changed by conc. hydrochloric acid.

From solutions of the dihydrochloride in water, the free leucobase, *i. e.*, the phenyldiaminophenol, may be precipitated by the addition of alkalis. The colorless crystals formed quickly oxidize in the air forming a brown product. The leucobase, insoluble in water, is soluble in strong alkalis and in acids.

V. Oxidation of 2-Phenylamino-4-aminophenol. The Preparation of



—On oxidation with ferric chlo-

ride this phenol gives a solution having the same violet-red color as those produced by the phenyldiaminophenol (IV) and the dimethyldiaminophenol (II).

Some 2-phenylamino-4-aminophenol-dihydrochloride (0.8 g.) in 40 cc. of 50% acetic acid at 0° was oxidized by 2.5 cc. of 4 *N* ferric chloride. A solution of 1.2 g. of picric acid in 16 cc. of glacial acetic acid was added to the deep violet solution. The resulting brownish solution was filtered from a slight precipitate. Then 150 cc. ice cold water was run in slowly, with stirring, to precipitate the picrate. Under the microscope small clusters of crystals were observed. The precipitate was collected, washed with cold dil. acid and finally with a little ice cold water. It was dried to constant weight. The yield was 75% of the theoretical.

Subst., 0.2612; CO₂, 0.4865; H₂O, 0.0752. Subst., 0.0852; 12.15 cc. dry N₂ at 10° and 742 mm.

Calc. for C₁₈H₁₃O₈N₅: C, 50.57; H, 3.07; N, 16.40. Found: C, 50.80; H, 3.22; N, 16.29.

The picrate swells up on being heated, evolving odors characteristic of picrates, leaving a residue very difficult to burn. It was necessary to replace the copper oxide by lead chromate in the determination of nitrogen.

The picrate is scarcely soluble in water, readily soluble in dilute acids, giving beautiful violet solutions. It is easily soluble with red color in alcohol, acetone, less soluble in chloroform. In conc. sulfuric acid an intense blue coloration is produced.

The salts of the phenylaminoquinonimine are very unstable in solution,

rapidly precipitating a black insoluble substance. Attempts to prepare the salts of the common inorganic acids have thus far failed due to their solubility and to rapid condensations. Even in the above picrate a small residue insoluble in dilute acids was found.

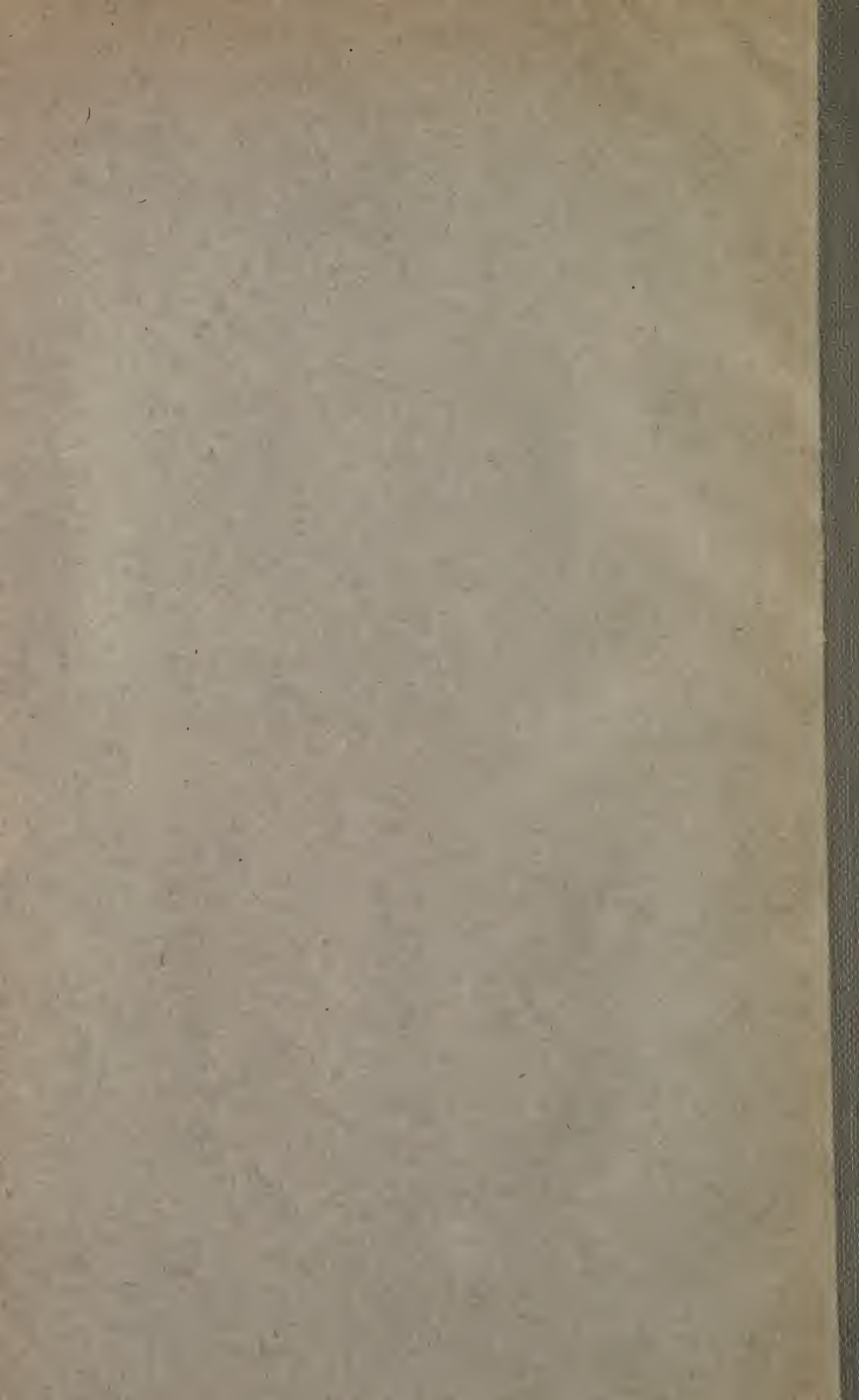
VI. Oxidation of 2,4,6-Triaminophenol.—The diaminoquinonimine hydrochloride¹ prepared by oxidation of this phenol was titrated with titanium trichloride, the values found agreeing with the assigned holoquinoid formula.

Summary.

In the aminoquinonimine salts the auxochromic effect of one phenyl-amino group is, unlike the cases of other holoquinoid salts, the same as the auxochromic effect of one dimethylamino group.

I wish to express my sincere thanks for the many helpful suggestions made by Dr. Jean Piccard, under whose able direction this work was carried out.

¹ Carl Heintzel, *Z. Chem.*, 1867, 342.



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